DIFFUSION MODEL FOR PLANT CUTICULAR PENETRATION BY SPRAY−APPLIED WEAK ORGANIC ACID BIOREGULATOR IN PRESENCE OR ABSENCE OF AMMONIUM NITRATE

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ABSTRACT. *Current agricultural crop management practices stand in need of more effective ways to enhance penetration by spray−applied systemic materials through rate−limiting, plant cuticular surfaces. A goal of this study was to develop a plant cuticular penetration model that may aid in identifying and quantifying factors in transcuticular transport that can be effectively managed to promote penetration. A diffusion model was developed that embodied a time−dependent diffusivity and an instantaneous plane source that simulated a finite−dose spray solution containing a systemic active ingredient, with and without an additive intended to increase penetration. The time−dependent, three−layer, apparent diffusivity model was intended to simulate a donor layer on the plant surface whose driving force changed with time owing to spray−droplet drying and alteration of active−ingredient properties by solution additives. The model was validated by comparing its predictions of cuticular−penetration with laboratory data for the anionic form of 1−naphthylacetic acid (NAA) in the presence and absence of ammonium nitrate (AMN), which increases NAA uptake. Data were obtained with a finite−dose diffusion cell under defined laboratory conditions. The model satisfactorily simulated the experimental observations over a time course of 120 h, other than a tendency to overestimate penetration during the first 10 h following application. Model results also support the possibility that AMN alters the anionic form of NAA to the more readily penetrating nondissociated form.*

Keywords. *Application technology, Bioregulator, Cuticle, Cuticular membrane, Diffusion, Diffusivity, Foliar, Penetration, Pest management, Surface, Systemic.*

Effective spray application is an essential cultural practice in crop production. The spray−application process consists of a series of complex interdependent events, namely, formulation of an active ingredient, atomization of the spray solution, transport of spray to the target plant surfaces, and droplet impaction, retention, residue formation and, for systemic agents, penetration into the plant. Particularly for systemic active ingredients, once they have been successfully delivered to the foliar surface, it remains to achieve effective delivery of that active ingredient to sites of action within the plant. At the same time, penetration rate should not be so great that phytotoxicity occurs and impedes further uptake. This work was intended to provide better understanding of key transport processes that govern cuticular penetration by systemic compounds, and their interactions with solution additives that improve uptake.

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PREVIOUS WORK

Bukovac and Petracek (1993) surveyed the use of isolated leaf and fruit cuticles in studying foliar penetration. They noted that the cuticle can be regarded as a non−living, lipoidal membrane that covers all aerial plant parts and as such is the interface between the plant and its environment. It is the prime barrier to penetration of pesticides, bioregulating compounds, and atmospheric pollutants deposited on the plant surface. Thus, isolated cuticles provide a physical system enabling transcuticular transport studies under defined conditions. They further noted that most work with isolated cuticles has focused on sorption, desorption, and infinite−dose cuticular transport of compounds in aqueous systems. It was shown how cuticular isolation methods and related work have made possible the determination of partition coefficients, thereby providing information on solubilities of various compounds in the cuticle, as well as permeance and diffusion coefficients. By comparing infinite−dose and finite−dose methods, they suggested that the finite−dose system was well suited for studying the effects of additives on transcuticular penetration from spray droplets and deposits on the surface.

Cuticular membranes of higher plants are composed of polyester matrices of hydroxy fatty acids embedded and covered with waxes, and serve as prime barriers to loss of water from plants as well as to penetration of substances applied or deposited on plant surfaces. Lieb and Stein (1971) suggested an analogy between diffusion across such biological membranes and transport through nonporous synthetic polymer membranes consisting of materials such as natural rubber or polyisobutylene. They examined methods for

membrane diffusivity measurement and suggested molecular mechanisms for diffusion in polymers.

Schönherr and Baur (1994) reported extensive investigations on plant cuticular penetration modeling and on the role of cuticular lipids, and determined values for permeances, partition coefficients, and diffusion coefficients. Knoche and Bukovac (1994, 2000) and Knoche et al. (2000a) reported on uptake of systemic compounds, identifying penetration through the cuticular membrane as the rate−limiting step in terms of conductance. By means of infinite− and finite−dose diffusion cells, they demonstrated effects of formulation additives and humidity on cuticular penetration of systemic pesticides. Their data included values for aqueous solution conductances and diffusivities and the effect of epicuticular waxes and surfactants on penetration.

As another example, Maschhoff et al. (2000) studied effects of ammonium sulfate on uptake and efficacy of glufosinate herbicide. At varying degrees for the series of weeds of economic importance used in the experiments, ammonium sulfate increased herbicide uptake and efficacy.

Schönherr and Baur (1994) showed that foliar−applied nonpolar pesticides can penetrate lipoidal membranes by diffusion. They also report that some spray additives, such as surfactants, can increase diffusion of active ingredients by plasticizing waxes or by solubilizing wax components of the cuticle.

Tamura et al. (2001) found, by fluorescence examination, that a nonionic octylphenoxypolyethoxy ethanol surfactant solubilized epicuticular wax of tomato fruit and broccoli leaves when present above the critical micelle concentration.

Bukovac et al. (2003) studied effects of ammonium nitrate (NH_4NO_3, AMN) adjuvant on penetration of 1−naphthylacetic acid (NAA) growth regulator, foliar−applied as 1 μL droplets, through enzymatically isolated tomato fruit cuticular membranes (CM) using a finite−dose diffusion system. Maximum penetration rate and total amount penetrated after 120 h served as measures of treatment effects. They found AMN (8 mM) increased NAA penetration significantly at pH values (5.2, 6.2) for the anionic molecular form, but had no effect at pH 3.2, indicating that the effect was primarily on the nondissociated molecular form. Ammonium sulfate and ammonium dihydrogen phosphate (both at pH 5.2) and alkylamine hydrochlorides were found equally effective as AMN, but potassium nitrate and calcium nitrate reduced NAA penetration compared to NAA alone. AMN had relatively a greater effect on NAA penetration through native, nondewaxed CM than through dewaxed CM. AMN effects were related to relative humidity (RH), being greater for both the penetration rate and total penetration at lower (<63%) than at higher (>64%) RH. Droplet drying and the presence of AMN and NAA together in the donor droplet or residue were found necessary for AMN enhancement of NAA penetration. They suggested that AMN presence in drying droplets or residues results in protonation of NAA anions, yielding nondissociated NAA, which penetrates readily. It was further suggested that volatilization of the ammonia produced, and penetration of nondissociated (free) NAA into the CM, favor continued formation of free NAA as long as NAA and AMN are available and conditions in the donor deposit support these reactions.

OBJECTIVE

The primary objective of this study was to develop a penetration model for foliar or fruit cuticles that can help identify and quantify key transport processes that govern cuticular penetration. Development of the current model was limited to simulating uptake of a weak organic acid, growth−regulating active ingredient with and without an ammonium salt additive. Specifically, the model will be applied to simulation of anionic NAA uptake alone vs. that with AMN additive, with no attempt to include humidity effects.

THEORY

The work by Cussler (1984) provides physical data on diffusion in gases, liquids, and solids and useful insights in theory for membrane transport processes. Carslaw and Jaeger (1959) and Crank (1956), in their reference works on mathematics of diffusion, outline solution methods for a wide array of diffusion problems, including transport through multiple layers of dissimilar substances and use of instantaneous sources.

In the current work, a one−dimensional, membrane diffusion model was developed for cuticular penetration of a bioregulator (NAA) applied as a finite−dose in a simulated aqueous spray droplets to a plant surface. While the physical spray application process and rough topography of plant surfaces may result in discontinuous, irregular deposit structures, it was assumed that the applied solution and its ultimate residue reside as a film of effective thickness x_0 on the epicuticular surface, which has its outer interface set at $x = x_0$. This can be justified only in the sense that the area covered is large relative to the film thickness. It was assumed that there was no loss of active ingredient at the surface $x = 0$, with solvent evaporation only at that surface, which sets the outer boundary condition for the diffusion model. Physically, this implies that after most of the solvent has evaporated, the film will continue as donor in the penetration process at a rate dependent on its ability to deliver NAA and the capability of the CM to transfer NAA.

The model was structured such that the cuticular membrane could, in principle, consist of two or more sublayers. Figure 1 shows a section of cuticular membrane overlaid with a donor layer. As depicted in figure 1, a spray−applied donor layer occupies the space $0 \le x \le x_0$ and is initially an aqueous solution containing the formulated active ingredient, possibly in the presence of an additive. The irregular contact interface shown in figure 1 is an idealization, since the donor layer may not be in complete contact at every point of the interface. This is an important factor, since it contributes to our assumption that the outermost layer of the membrane, the epicuticular wax (ECW) layer, is a prime barrier to penetration. In figure 1, the donor layer overlays the ECW layer of thickness $x_1 - x_0$, which in turn overlays a cutin matrix layer of thickness $x_2 - x_1$ containing an embedded cuticular wax (CW) layer, adding up to a total cuticular membrane thickness of $x_2 - x_0$. The ECW layer thickness is typically considered to be only about one−tenth of the total cuticular membrane thickness (Schönherr and Baur, 1994). Later in the development, the ECW, CW, and cutin matrix diffusivities are combined in such a way that a specific value for x_1 does not appear in the model. For the purposes of this

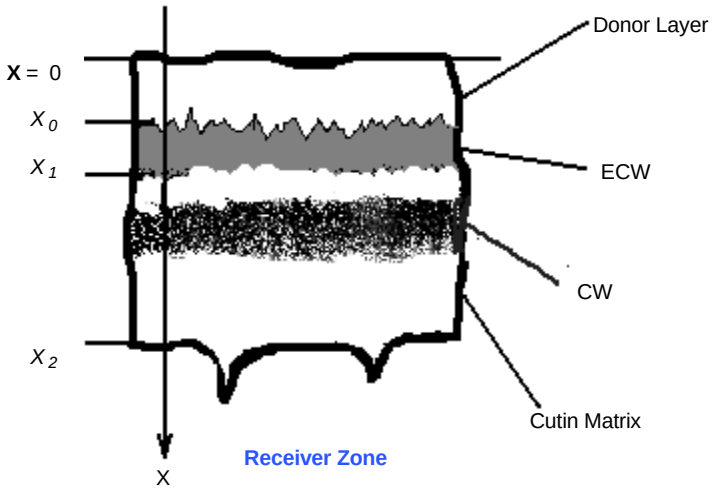

Figure 1. A sketch of a section of cuticular membrane with an applied donor layer and showing the membrane sublayers consisting of epicuticular wax (ECW) and the cutin matrix with internal layer of cuticular wax (CW).

model, while the CW layer contributes to the resistance of the membrane to penetration, the CW and cutin matrix interpenetrate to the extent they are considered a single layer. The ultimate goal for the model was to simulate accumulation of diffusing active ingredient arriving at $x = x_2$ during a period of time *t*. Beyond $x = x_2$, the inner boundary of the membrane, it was assumed that NAA molecules were effectively swept away to their sites of action in the plant. In the laboratory diffusion cell, this process was simulated by transfer of NAA through the membrane into a very dilute aqueous solution beyond $x = x_2$. For the diffusion model, the mathematical task was summation of parcels of NAA molecules as they arrived at $x = x_2$, a flux integration operation.

Since there is a film (droplet) drying period, and partitioning of NAA molecules into an ideally "empty" membrane structure takes place as transport progresses, the diffusion coefficient was assumed to be time dependent. In some cases not to be considered here, there may be physical changes in the membrane transport properties due to the solution, additives, or other effects (e.g., surfactant solubilization of cuticular waxes). This suggested a diffusion model of the form:

$$\frac{\partial c(x,t)}{\partial t} = \kappa(t)\frac{\partial^2 c(x,t)}{\partial x^2} \qquad (1)$$

The nomenclature section at the end of this article lists the functions, parameters, and variables used in the model development. It is important to realize that varying degrees of heterogeneity may exist in the donor layer, in membrane structure, or in their uniformity of contact, and that these factors may change with time during the course of a transport process. Diffusion models inherently tend to smooth irregularities and effectively simulate transport processes that are to an extent random.

It was assumed that as the donor layer dries and transport conditions stabilize, transcuticular resistance would increase to a degree over a significant period of time. Hence, a continuously decaying diffusion−coefficient model was hypothesized of the form:

$$\kappa(t) = \kappa_f - (\kappa_f - \kappa_i)e^{-t/\theta} \qquad (2)$$

A potential limitation of this model is that the driving force, and hence the initial transport rate, may be lower due to the relatively more dilute state of the spray solution at application. As solvent (in this case water) evaporates from the donor layer, solute concentration in the layer will increase as it approaches a hydrated state, when there would be a corresponding decrease in solute mobility. Under such conditions, the transport rate might initially increase, pass through a peak, and then decrease with time as it approached equilibrium.

In modeling transport resistance of plant cuticles, one may note that Knoche et al. (2000b) determined partitioned conductances and resistances for components of sweet cherry cuticular membranes. Earlier, Schönherr and Baur (1994) drew similarities between molecular transport in a cuticular membrane and conduction of electrons in a wire. Thus, drawing on the analogy of several resistance elements in series in an electrical circuit, it was assumed, e.g., that the total resistance to long−term transport from the donor layer through a two−layer membrane, as shown in figure 1, could be written as a sum:

$$R_f = R_0 + R_1 + R_2 \qquad (3)$$

Note that R_2 is a combination of the resistances of the cutin matrix layer and its interpenetrating CW layer. Diffusion coefficients are inversely proportional to the substrate mass density and its resistance to transport of, and the partition coefficient for, the diffusing substance in that substrate, in the form:

$$\kappa_n \propto 1/\rho_n R_n K_n \qquad (4)$$

Upon application of equation 3, it was consequently inferred that a long−term, apparent diffusion coefficient for the combined donor and cuticular layers could be estimated by means of the result:

$$\kappa_f = \frac{\kappa_0\kappa_1\kappa_2}{\kappa_0(\kappa_1 + \kappa_2) + \kappa_1\kappa_2} \qquad (5)$$

A similar form was presumed for the initial apparent diffusivity, by replacing κ_f with κ_i, and κ_0 with κ_s, an effective diffusivity for the donor layer in its initial liquid state. It must

be cautioned that this particular diffusivity model does not account for differences in thickness among the layers. Owing to the uneven configuration of the interfaces and lack of definitive data, it was not possible to include this factor pending further research.

Crank (1956) suggested a transformation for time−dependent diffusion coefficients which, when applied to equation 2, gives the result:

$$\tau = \tau(t) = \int_0^t \kappa(\xi)d\xi = (\kappa_i - \kappa_f)\theta\left(1 - e^{-i/\theta}\right) + \kappa_f t \quad (6)$$

with equation 1 becoming:

$$\frac{\partial v(x,t)}{\partial t} = \frac{\partial^2 v(x,t)}{\partial x^2} \quad (7)$$

The unit instantaneous plane source (Carslaw and Jaeger, 1959), which is inherently a solution of equation 7, can be used to simulate diffusion of a unit amount of substance (a finite dose) deposited on a plane surface at $x = 0$ at $\tau = 0$ ($t = 0$, $\tau = \tau(0)$):

$$f(x,\tau) = \frac{e^{-x^2/4\tau}}{2\sqrt{\pi\tau}} \quad (8)$$

For the purposes of this model, the unit source was placed at the surface $x = x_0$, the critical interface between the thin donor layer and the cuticular membrane. The time−dependent diffusion coefficient enabled flexibility in controlling, and thereby modeling, the rates at which the instantaneous source can deliver and the membrane can receive molecules. The boundary condition that no transport occur across the plane $x = 0$ was imposed by superposing an identical image source at $x = -x_0$. Thus, an instantaneous unit source function was defined as:

$$u(x_2 - x_0, \tau) = f(x_2 - x_0, \tau) + f(x_2 + x_0, \tau) \quad (9)$$

referred to $x = x_0$ and specialized to express the amount of diffusing substance arriving at $x = x_2$ at $\tau(\tau = \tau(t))$, effectively defining a flux.

The next task was to determine the cumulative amount of substance (NAA) entering the plant site of action, simulated in the laboratory by the diffusion cell receiver zone. This required an integration of equation 9 over the interval $0 \le \xi \le \tau = \tau(t)$:

$$v(x_2 - x_0, t) = v_0 \int_0^{\tau=\tau(t)} u(x_2 - x_0, \xi)d\xi \quad (10)$$

and introduction of the normalization coefficient (v_0).

A solution for equation 10 was obtained by integrating equation 9 termwise. The first step was to obtain the Laplace transform of equation 8:

$$L\{f(x,\tau)\} = \frac{e^{-\sqrt{px}}}{2\sqrt{p}} \quad (11)$$

where p is the transform parameter. The Laplace transform of the integral of equation 8 can be obtained by dividing equation 11 by p to get:

$$L\left\{\int_0^\tau f(x,\xi)d\xi\right\} = \frac{e^{-\sqrt{px}}}{2p^{3/2}} \quad (12)$$

The inverse transform of equation 12, tabulated in Carslaw and Jaeger (1959), in combination with equations 9 and 10 gives the fundamental expression for accumulated penetrant:

$$v(x_2 - x_0, t) = \left\| v_0\{4\tau[f(x_2 - x_0, \tau) + f(x_2 + x_0, \tau)]\} - v_0(x_2 - x_0)erfc\left[\frac{x_2 - x_0}{2\sqrt{\tau}}\right] - v_0(x_2 + x_0)erfc\left[\frac{x_2 + x_0}{2\sqrt{\tau}}\right]\right\|_{\tau=\tau(t)} \quad (13)$$

As indicated, the result given by equation 6 for τ must be inserted into equation 13 to complete the solution.

Comparison with Laboratory Results

Predictions from the model (eq. 13) were compared with laboratory data obtained with cuticular membranes enzymatically isolated from 'Pik Red' tomato fruit selected to be free of visual defects and grown without use of pesticides, as described by Bukovac et al. (2003). Isolated cuticles were air dried, and disks of 17 mm diameter weighing 2.28 to 2.90 mg were removed with a cork borer, mounted in finite−dose diffusion cells, and leak tested before use. Radio−labeled NAA {[^{14}C]−NAA (2− (1−naphthyl) [1−^{14}C] acetic acid)} solutions were prepared at 215 μM concentrations and titrated with HCl to pH 5.2. For treatments using AMN with NAA, AMN concentration was 8 mM. To simulate spray droplets, solutions were applied to CM with a repeating microsyringe, three 1 μL drops for each CM specimen. Three mL of distilled, deionized water (pH 5.2) each served as receiver solution for each CM, with six replications of each treatment. Experiments were performed in growth chambers or a temperature−controlled laboratory at 24.0°C. Relative humidity, which was not controlled and varied from 28% to 32%, was at a sufficiently low level to minimize interaction with AMN and better isolate AMN effects on uptake (Bukovac et al., 2003). The receiver solutions were monitored at periodic intervals from 0 to 120 h. Time−course curves were constructed for the laboratory part of the experiments The initial penetration rate and the total amount of penetration after 120 h were used as indices of penetration (Knoche et al., 2000a).

Parameters used for the model simulations are listed in table 1. As indicated, the component diffusivities are given for each apparent diffusivity (κ_i or κ_f) as in equation 5 for both cases: NAA alone and NAA with AMN. For either case, the values for κ_s under κ_i fall in the range of diffusivities for organic substances in water, as listed by Cussler (1984, p. 116, table 5.2−1). As shown in table 1, validation trials revealed that values for κ_0 with this diffusivity model needed to be reduced by about five orders of magnitude from those for κ_s in expectation that the donor layer eventually would become a hydrated residue and would continue to act as

donor, but at a dramatically lower rate. The existence of a hydrated state of the residue is further supported in that the penetration rate increases or decreases with corresponding changes in ambient humidity. This will be the case with or without AMN present. Diffusivity values for κ_1 or κ_2 are in the range of those reported by Knoche and Bukovac (1994) for cuticular membranes. It is presumed that κ_1 has the least value in its group on the *a priori* assumption that the ECW is a prime barrier to penetration. All coefficients are presumed larger as transport begins. As transport proceeds, it is expected that AMN has altered the state of NAA to a more readily penetrating molecular form, as indicated from the studies of Bukovac et al. (2003). While anionic NAA can penetrate, it does so much less readily than the nondissociated molecular form of NAA. It is assumed that AMN had no significant effect on the structure of the ECW, CW, or cutin matrix and, therefore, minimal effect on their intrinsic transport properties, as reflected in the values for κ_1 and κ_2 in table 1. It should also be noted that the normalization coefficient (v_0) has the same value with or without AMN present.

The hypothesized decaying−exponential, time−dependent diffusivity (eq. 2) was in part based on an anticipated droplet drying process. However, the time constant (θ) of equation 2 must ultimately reflect lags in the onset of transport, partitioning in the membrane, and the underlying molecular diffusion process itself, and semi−empirical values obtained for θ in this study support these expectations. Spray additives, such as AMN, may alter properties and/or the microenvironment of the donor deposit, effectively increasing diffusivities, as apparently occurred in this study. In other cases not considered here, some additives, e.g., surfactants of certain types with relatively small ethoxy (EO) number, may penetrate the cuticle and effect changes in the biomembrane structure that subsequently reduce time constant values and increase diffusivities. In contrast, in sufficient concentration, some surfactant micelles may impede uptake by capturing active ingredient molecules.

Insofar as model equations 2 and 5 may be valid, the simulation indicates a degree of dependence of penetration rate on changes over the course of time in the apparent diffusivities (κ_i or κ_f) and the component diffusivities (κ_s and κ_0) in the donor layer, and κ_1 and κ_2 in the epicuticular and cuticular layers. While some effect was predicted for NAA penetration alone, a stronger effect was anticipated for penetration of NAA in the presence of AMN additive, suggesting alteration of NAA to the more readily penetrating nondissociated form (Bukovac et al., 2003; Schönherr et al., 2000) or possibly some additional deliquescence effect.

Table 1. Model parameters used for NAA cuticular penetration simulations alone and with 8 mM concentration NH_4NO_3.

Parameter	NAA Only	NAA + NH_4NO_3
v_0	1675	1675
x_0 (μm)	5	5
x_2 (μm)	15	15
θ (h)	120	24
κ_i (cm²/s)	4.5×10^{-10}	5.0×10^{-9}
κ_s[a]	1.0×10^{-5}	1.0×10^{-5}
κ_1[a]	5.0×10^{-11}	5.5×10^{-9}
κ_2[a]	4.5×10^{-9}	5.5×10^{-8}
κ_f (cm²/s)	0.385×10^{-11}	0.645×10^{-11}
κ_0[a]	1.0×10^{-10}	2.0×10^{-10}
κ_1[a]	0.5×10^{-11}	1.0×10^{-11}
κ_2[a]	2.0×10^{-11}	2.0×10^{-11}

[a] Component diffusivities of the preceding κ_i or κ_f as in equation 5.

Figure 2 is a comparison of model simulations and experimental data for NAA alone and NAA with AMN, based on accumulation of diffusing solute arriving at the receiver solution at $x = x_2$. Agreement is satisfactory overall, except that in both cases a higher penetration rate is predicted during the first 10 h after application. Three possible factors may contribute to an initial overestimate of penetration, any one or all of which could occur. The first is that the standard diffusion equation is by default based on an assumption of a theoretically infinite velocity of propagation. This simply means that the diffusion equation predicts an instant concentration increase everywhere in the region of interest, however small, as soon as the transport process begins. This factor is probably least likely to be significant. The second factor is that the current time−dependent diffusivity model is of uniformly decaying form from the time transport begins. A model may be needed such that as the process begins and time progresses, the diffusivity starts at a relatively low value, increases to a peak, and then decays uniformly with time, as was suspected in the model development. This type of model would simulate an initial increase in solute concentration as solvent evaporated, followed by a gradual transition to a hydrated residue state with a slower transport rate. The third possible factor is that some number of labeled molecules must accumulate in the receiver for them to be detected. The normal requirement is that a reliable count should be twice the background level. Background count for the system used in this study was about 21 counts per minute (cpm), so sufficient radioactive molecules must have accumulated for one to conclude that transport activity has occurred. Thus, the time required for at least 42 molecules to accumulate is not addressed by the isotope detection technique, although it is more sensitive than any other available system. From figure 2, it would appear that the model predicts an immediate onset of penetration starting from $t = 0$. However, figure 3 shows model behavior over the initial 0.4 h and demonstrates a lag in onset of penetration that is not evident in figure 2, as indicated by a gradual increase in transport rate with time as the uptake process begins.

CONCLUSIONS

The current model is an attempt to model the effect of an ammonium salt additive on a systemic, weak organic acid bioregulator. Comparisons of laboratory data with predicted penetration rates from the model (eq. 13) indicate satisfactory agreement over the experimental time course of 120 h. However, for the first 10 h of penetration, the model predicts a higher uptake rate than the data indicate. This may be due in part to the possibility that a uniformly decaying, time−dependent diffusivity model, as represented by equations 2 and 5, does not adequately allow for an initially lower transport rate until the effective concentration in the donor layer reaches a level that provides a stronger driving force. Hence, it would not fully account for the solution dynamics. Insofar as they can, the diffusivity parts of the model appear to offer ways to implement submodels for interactions among solute, solvent, and additives producing physical or chemical structural changes in either the donor layer or the membrane,

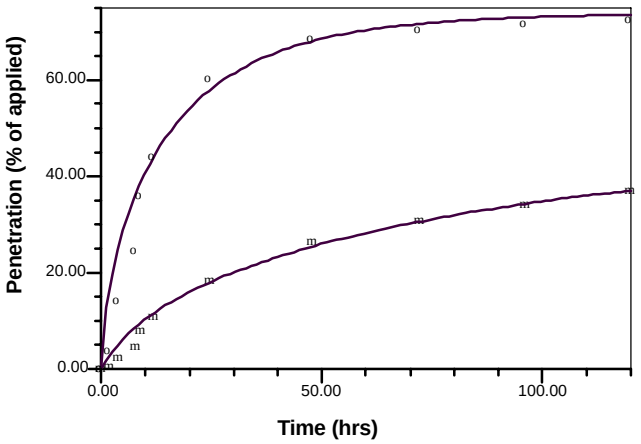

Figure 2. Comparison of cuticular penetration model (eq. 13) simulations (solid lines) with laboratory data obtained with a finite−dose diffusion cell for NAA alone (circles) and for NAA with 8 mM AMN (m's), with relative humidity in the range 28% to 32%.

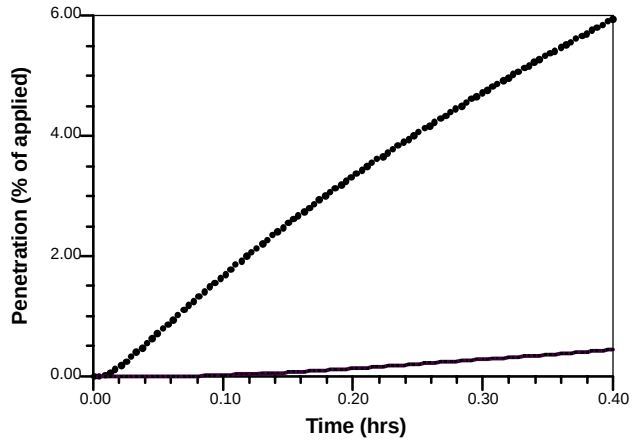

Figure 3. Behavior of the penetration model (eq. 13) at short diffusion times for NAA alone (line) and NAA with 8 mM AMN (dots), with relative humidity in the range 28% to 32%. An increase in slope can be seen in the model simulation as the penetration process begins, indicating a lag in onset of transport.

which may accelerate (or impair) uptake. This suggests applications beyond the current case of AMN additive that works a transformation of anionic NAA in the donor layer.

In future research, use of superposed instantaneous point sources would enable modeling discontinuous, nonuniform distributions of active ingredient in donor layers. A diffusivity model that better represents the course of donor layer changes of state and thicknesses of cuticular layers should be investigated. Other important effects to be accounted for in future model developments should address factors including variations in humidity, pH, and temperature.

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Nomenclature

$c(x,t)$ = mass of diffusing substance at x at time t (% of applied dose)
$f(x, \tau)$ = unit instantaneous plane source function (cm^{-1})
K_n = partition coefficient, nth layer (dimensionless)
R_0 = donor layer transport resistance (cm∗s/mg)
R_1 = ECW layer transport resistance (cm∗s/mg)
R_2 = combined CW and cutin matrix layer transport resistance (cm∗s/mg)
R_f = total long−term cuticular transport resistance (cm∗s/mg)
R_n = nth layer transport resistance (cm∗s/mg)
t = time (s)
x_0 = thickness of donor layer (μm or cm)

$x_1 - x_0$ = thickness of ECW layer (μm or cm)
$x_2 - x_1$ = thickness of combined CW−cutin matrix layer (μm or cm)
θ = time constant (s)
$\kappa(t)$ = time−dependent diffusion coefficient (cm^2/s)
κ_0 = limiting (final) donor layer apparent diffusion coefficient (dried semi−solid state) (cm^2/s)
κ_1 = ECW layer diffusion coefficient (cm^2/s)
κ_2 = combined CW and cutin matrix layer apparent diffusion coefficient (cm^2/s)
κ_i = initial apparent cuticular diffusion coefficient (cm^2/s)
κ_f = limiting (final) apparent cuticular diffusion coefficient (cm^2/s)
κ_n = *n*th layer diffusion coefficient (cm^2/s)
κ_s = initial donor−layer apparent diffusion coefficient (liquid−solution state) (cm^2/s)
$\nu(x,t)$ = mass of diffusing substance at x at time t (% of applied dose)
ν_0 = normalization coefficient (% of applied dose × cm^{-1})
ρ_ν = mass density of *n*th layer (mg/cm^3)
τ = time−dependent transform variable (cm^2)